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13. ABSTRACT (Maximum 200 words)

The essence of the research consists of synthesizing unsaturated, chloro-functionalized carbosilanes or carbosiloxanes as a backbone polymer, and recent work with model compounds suggests that these syntheses will be successful. These chlorofunctionalized backbone polymers will be converted into either solvent resistant elastomers or high Tg materials via nucleophilic grafting reactions, chemistry which is reminiscent of the work done with polyphosphazene backbones. Thus, the goals of this research are:

to synthesize a variety of unsaturated polycarbosilanes and carbosiloxanes functionalized with the silicon-chlorine bond,

to graft low and high molecular weight sidechains on these backbones to tailor their physical behavior to specific needs, and,

to demonstrate that these polymers can be recycled via depolymerization.

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As is normally the case, full structural characterization work will accompany all phases of this research. A successful effort will lead to the creation of recyclable materials for a variety of applications including lubricants, face masks, high performance engineering plastics, coatings, and self lubricationg plastics. The final report summarized the research results.

***Chain Propagation/Step Propagation Polymerization Chemistry.
The Preparation of Solvent Resistant, Well Phase-Separated
Thermoplastic Elastomers***

FINAL REPORT

Prepared by
K. B. Wagener

September 30, 1993

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and
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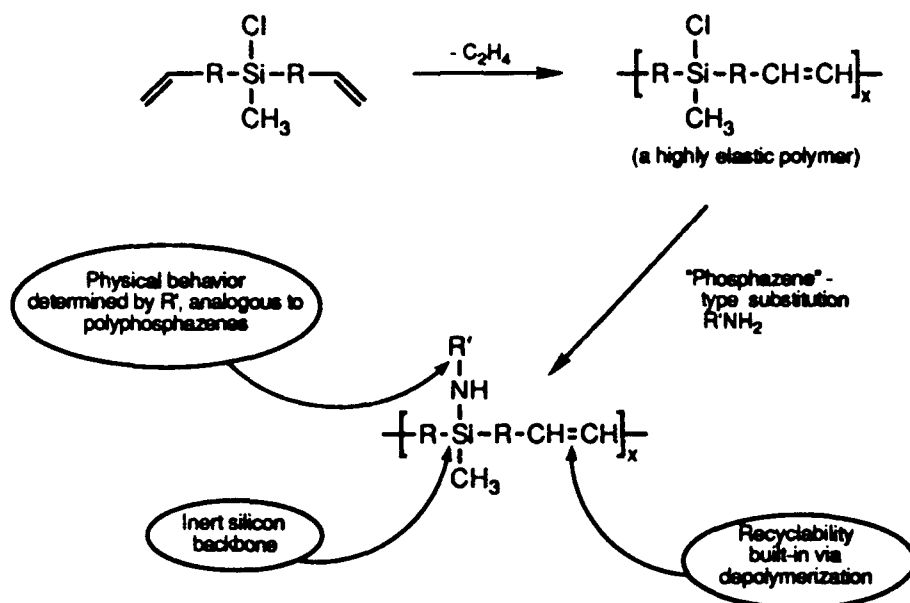
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THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

I. Abstract and Project Goals

Chain propagation/step propagation polymerization is a synthetic scheme designed by us some time ago to create polymers of well defined structure (see Addendum on page 9 for relevant publications). The work has led to a better understanding of the molecular requirements for phase separation in polyester ether, polysiloxane ester and most recently polysiloxane amide multiphase polymer systems. The silicon based materials have proven most interesting, and we propose to explore two classes of silicon-containing graft copolymers - unsaturated carbosilanes and unsaturated carbosiloxanes - in the synthesis of solvent resistant elastomers and high performance polymers. Polymer behavior will be determined by the type of graft used to form the copolymer.



The essence of the proposal, illustrated above, consists of synthesizing unsaturated, chlorofunctionalized carbosilanes or carbosiloxanes as a backbone polymer, and our recent work with model compounds suggests that these syntheses will be successful. These chlorofunctionalized backbone polymers will be converted into either solvent resistant elastomers or high Tg materials via nucleophilic grafting reactions, chemistry which is reminiscent of the work done with polyphosphazene backbones. Thus, the goals of this research are:

- to synthesize a variety of unsaturated polycarbosilanes and carbosiloxanes functionalized with the silicon-chlorine bond,
- to graft low and high molecular weight sidechains on these backbones to tailor their physical behavior to specific needs, and,
- to demonstrate that these polymers can be recycled via depolymerization.

As is normally the case, full structural characterization work will accompany all phases of this research. A successful effort will lead to the creation of recyclable materials for a variety of applications including lubricants, face masks, high performance engineering plastics, coatings, and self lubricating plastics.

FINAL REPORT

A. Human Resources Development. Prior experience has shown that one of the most important rewards of conducting academic research comes from training undergraduates, graduate students, and postdoctoral fellows in the multidisciplinary field of polymer chemistry. Thus far this ARO sponsored research has trained twelve such students, and each has moved on to productive lives in society. The breakdown is shown below:

Undergraduates	3
Graduate Students	7
Postdoctoral Associates	2

Further, nine of these students are of American origin, and two of them are minority candidates. The three foreign born students have been among the best students we have had at the University of Florida, one of whom has returned to his native country as a Professor of Chemistry. More details regarding their productivity can be found in the Addendum on page 9 of this report.

B. Chain Propagation/Step Propagation Chemistry. Multiphase polymers have played an important commercial role in today's society, ^{1,2} and there have been numerous investigations into factors influencing the physical behavior of these materials.^{3,4} Several years ago we initiated research in chain/step polymerization to elucidate factors associated with phase separation. The chemistry is illustrated in Figure 1 for the synthesis of polyester ether multiphase polymers, ⁵⁻⁷ where the goal has been to achieve complete phase separation in these polymer systems. We have done so by systematically varying the length of each segment present in these copolymers, and as a consequence we have been able to state unequivocally the requirements for complete phase separation in these materials.

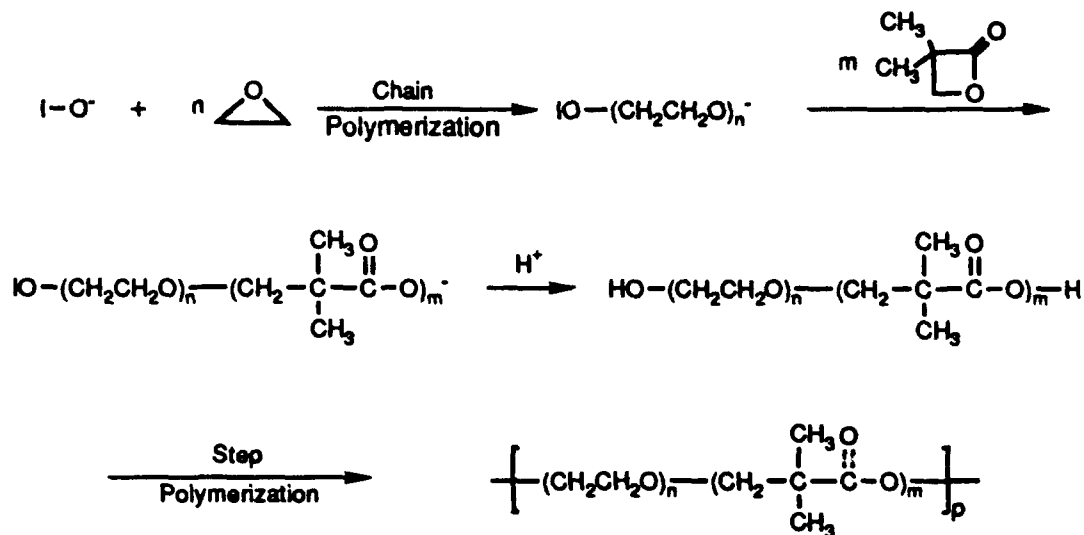


Figure 1. Chain/Step Synthesis of Poly(oxyethylene-co-pivalolactone).

Completely phase separated polyester ether elastomers can be synthesized via chain/step polymerization by choosing the proper length for each segment and by eliminating the defects present in the original anionic initiator system. A sample oligomer, which was synthesized in order to achieve the objectives of this study, is shown in Figure 2.

In this case, the polyether segment has been systematically increased in length while holding the polyester segment⁸ constant in length, and it is observed that complete phase separation exists when polyether repeat unit degree of polymerization has a value of 23 or higher.^{9,10} With this knowledge in mind, and with the design and synthesis of a new series of tailored masked anionic initiators,^{11,12} it has been possible to synthesize high molecular weight versions of these polymers.

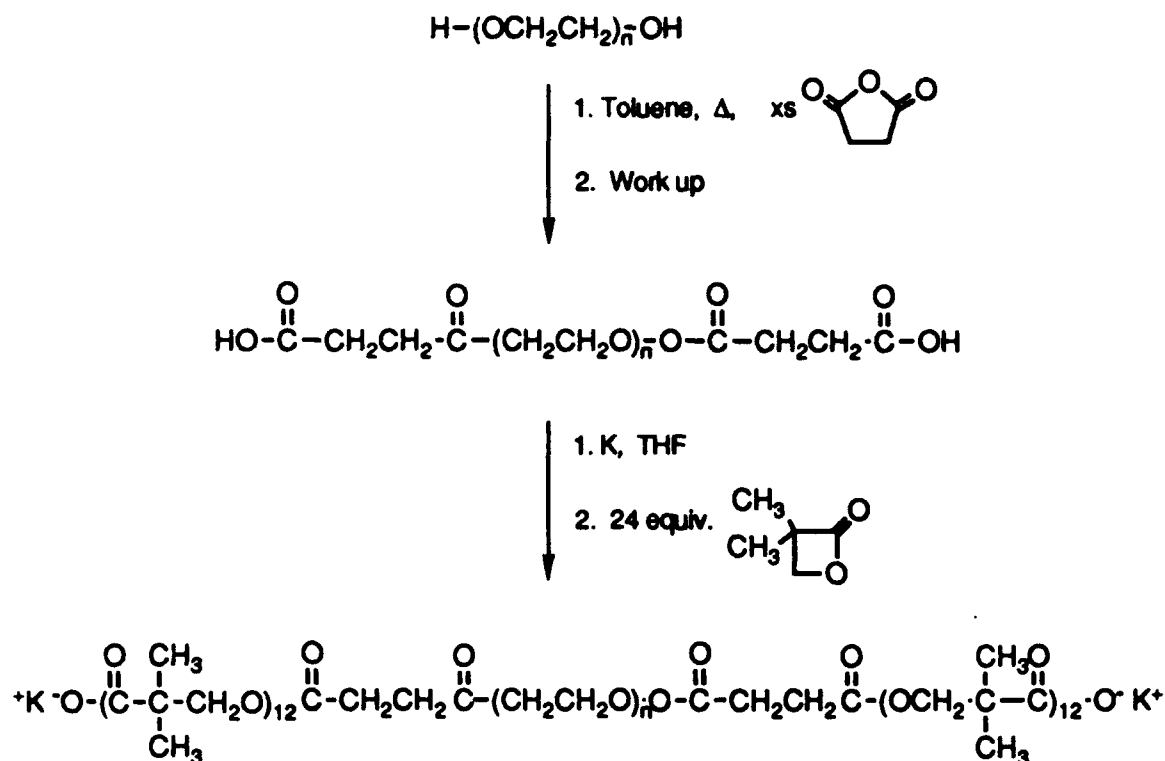


Figure 2. Reaction Scheme for the Synthesis of Triblock Poly(oxyethylene-co pivalolactone)Oligomers. The oxyethylene degree of polymerization, n , was varied to achieve complete phase separation.

C. Extension of this Research to Siloxane Based Thermoplastic Elastomers.

While polyester ether polymers are well known multiphase materials used on a large scale, silicon based materials, including Weber's carbosilane polymers, are equally as interesting.¹³⁻¹⁹ Consequently we extended our research to the synthesis of poly(siloxane)/polyester based elastomers using the reaction scheme shown in Figure 3. In this scheme, a rather conventional poly(siloxane) copolymer was used as a backbone in the grafting of pivalolactone as a hard phase.^{20,21} Our research has shown that phase separation is almost instantaneous and that solvent resistant elastomers are the result. The polymers are clean, easy to synthesize, and because of their potential utility, their physical behavior has been investigated as well. These materials have been patented²² and are available license-free to the Army.

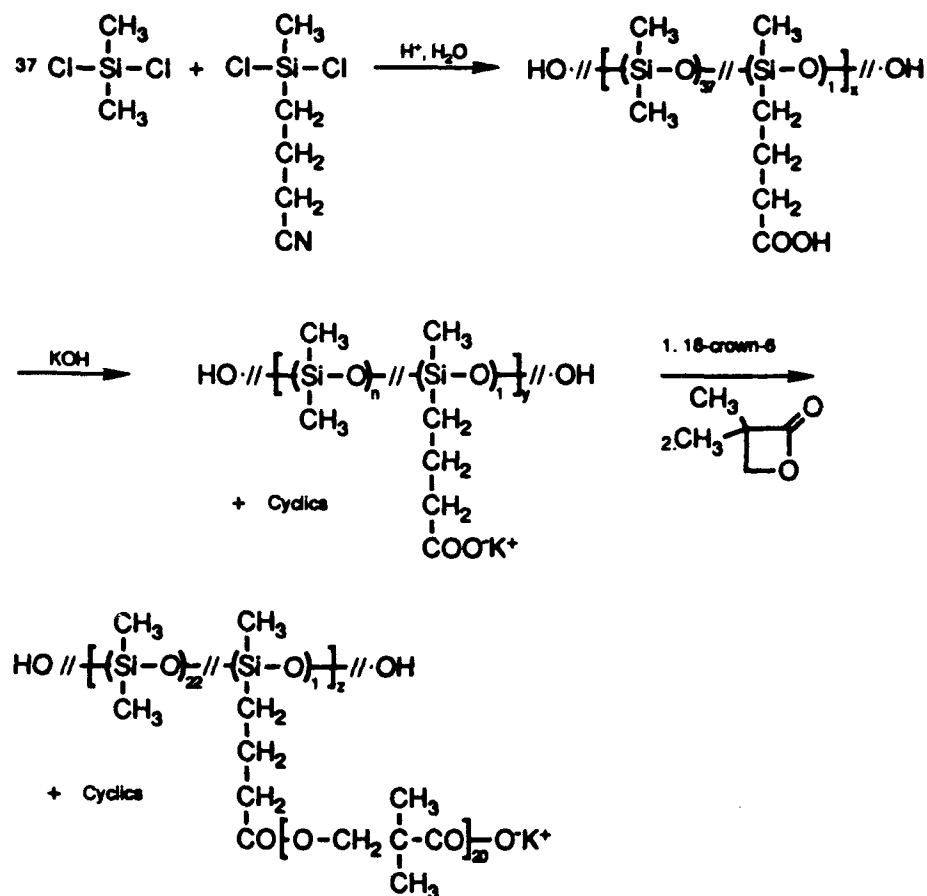


Figure 3. The Synthesis of a Siloxane - Ester Graft Copolymer

Further, the polyamide version of these copolymers has been synthesized through the grafting of caprolactam to this functionalized poly(siloxane) backbone, chemistry which is illustrated in Figure 4.^{23,24} We have found that only a low mol percentage of caprolactam can be incorporated in this siloxane-based copolymer structure. As a consequence, these materials are best described as surface-modified polyamides. The materials feel much like Teflon™ since much of the siloxane phase is deposited on the surface (XPS data). Since they remain thermoplastic, we describe them as self-lubricating thermoplastic elastomers.

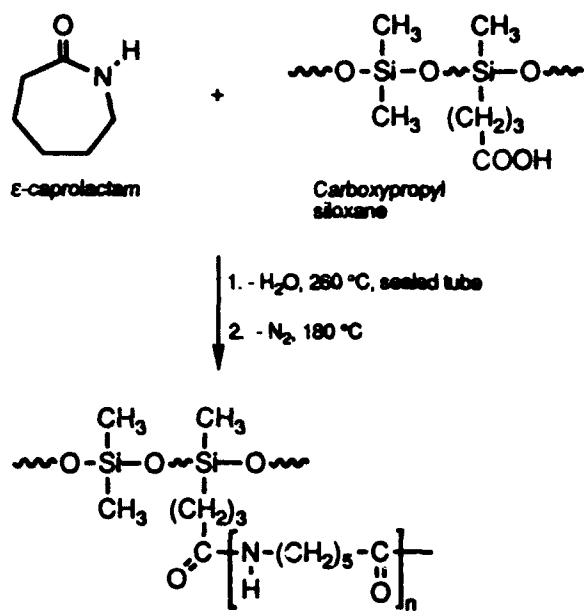


Figure 4. The Synthesis of a siloxane-caprolactam graft copolymer.

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ADDENDUM

Publications/Patents/People Trained with Prior ARO Support

A. <u>People Trained:</u>	<u>Undergraduates</u>	<u>Graduate Students</u>	<u>Postdocs</u>
	David Plevey Peter Orizondo Melanie Shepherd	Sophia Cummings Chris Marmo Chris Matayabas Dinesh Patwardhan Jason Portmess Dennis Smith Fabio Zuluaga	Dr. S. Wanigatunga Dr. C. Bauch

B. Dissertations and Theses:

Fabio Zuluaga, Ph.D. 1993, "Chemistry of Poly(ether-ester) and Siloxane Based Thermoplastic Elastomers"

Chris Matayabas, Ph.D. 1991, "Synthesis and Characterization of Regular Segmented Copolymers of Poly(pivalolactone) and Poly(oxyethylene)"

Dinesh Patwardhan, Master's 1991, "Synthesis and Characterization of Graft Copolymers Poly(siloxane-g-pivalolactone)"

Chris Matayabas, Master's 1988, "A Model Study of Microphase Separation in Triblock Poly(oxyethylene-co-Pivalolactone): Effects of Soft Segment Length"

C. Publications:

25. S. Wanigatunga, F. Zuluaga and K. B. Wagener, "Poly(siloxane) Graft Copolymers", a review in *Trends in Polym. Sci.*, Elsevier Publishing, submitted 1993.
24. J. C. Matayabas, Jr., and K. B. Wagener, "Quantitative Determination of Microphase Separation: Effect of Hard-Segment Lengths", *Macromolecules*, **25**, 1992, 5591.
23. J. C. Matayabas, Jr. and K. B. Wagener, "Chain Propagation/Step Propagation Polymerization: Synthesis of Defect-Free Telechelomers", *Macromolecules*, **25**, 1992, 5585.
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D. Patents:

K. B. Wagener and S. Wanigatunga, "Siloxane-Polypivalolactone Thermoplastic Elastomers", U.S. Pat. #4,985,511, Jan. 15, 1991.